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Organic Capillary Electrophoresis Analysis System (OCEANS) Subsystem of the European Molecular Indicators of Life Investigation (EMILI)

Peter A. Willis[1], M. Fernanda Mora[1], Jessica S. Creamer[1], Aaron Noell[1], Florian Kehl[1], Konstantin Zamuruyev[1], Mauro Sergio Ferreira Santos[1], Tony Ricco[2], Richard Quinn[2], Jennifer Stern[3], and William Brinckerhoff[3]

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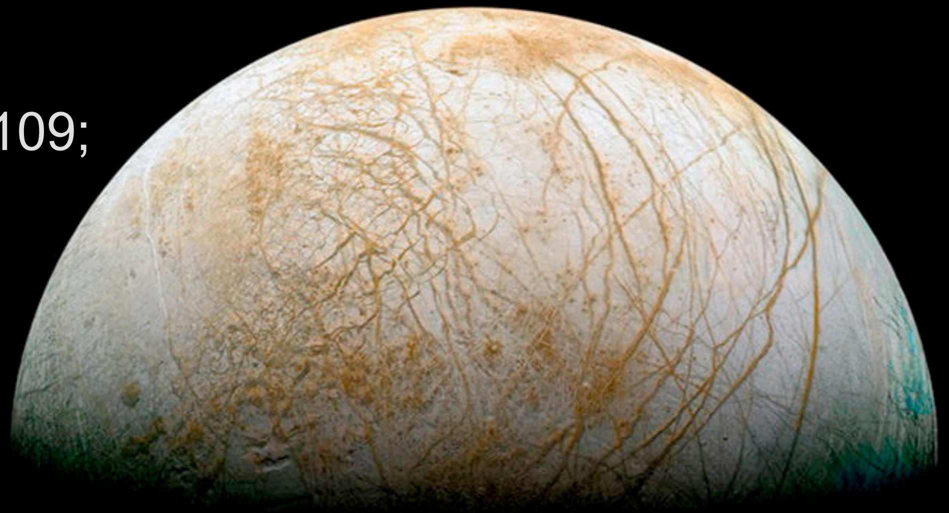
[2]NASA Ames Research Center, Moffett Field, CA 94035;
[3]NASA Goddard Space Flight Center, Greenbelt MD 20771.



AbSciCon 2019 Talk, 2:00PM, June 27, 2019

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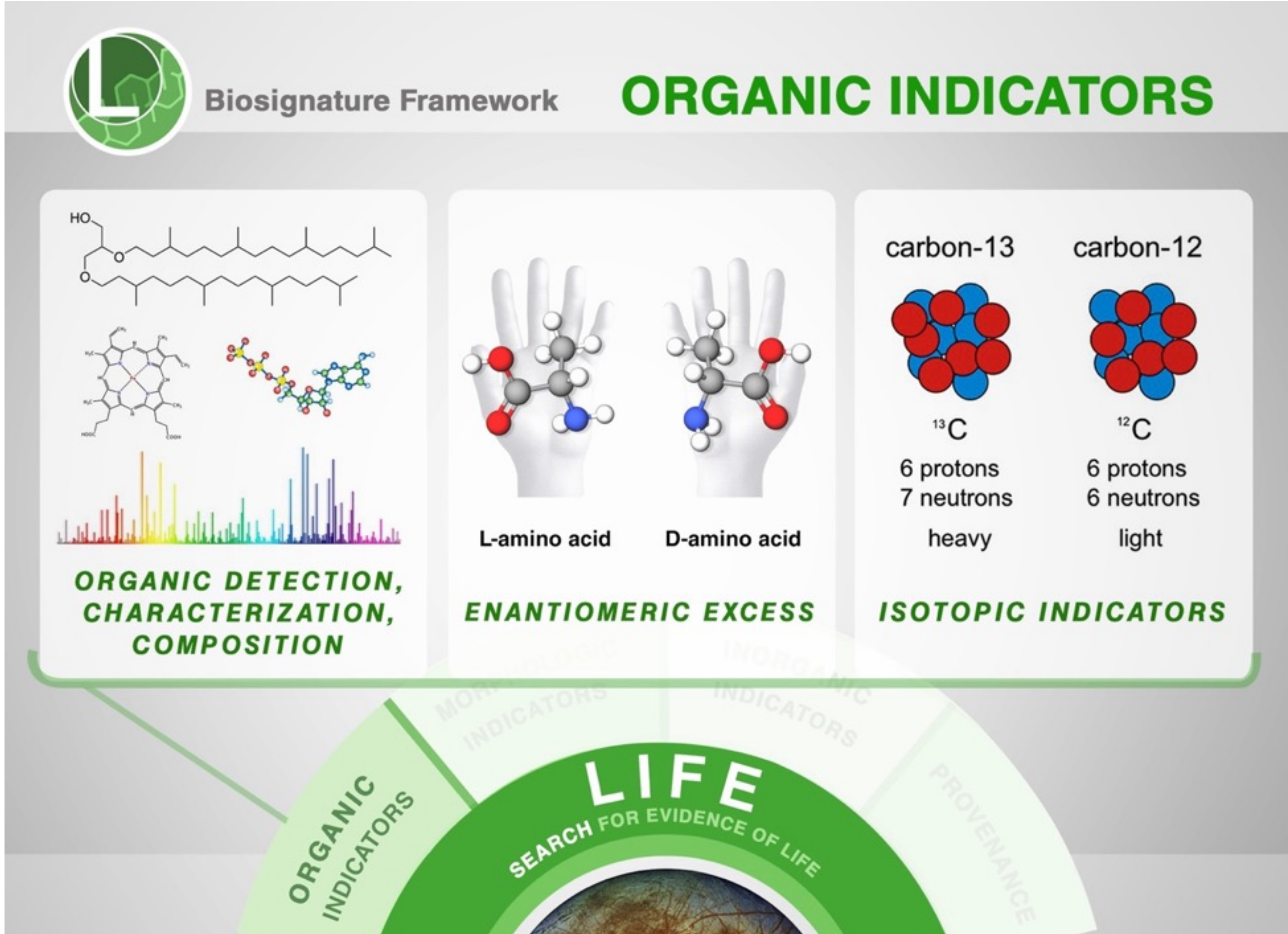
Outline

I. Architecting An Organic Chemical Analyzer for a Europa Lander Mission: EMILI

II. Key Developments at JPL

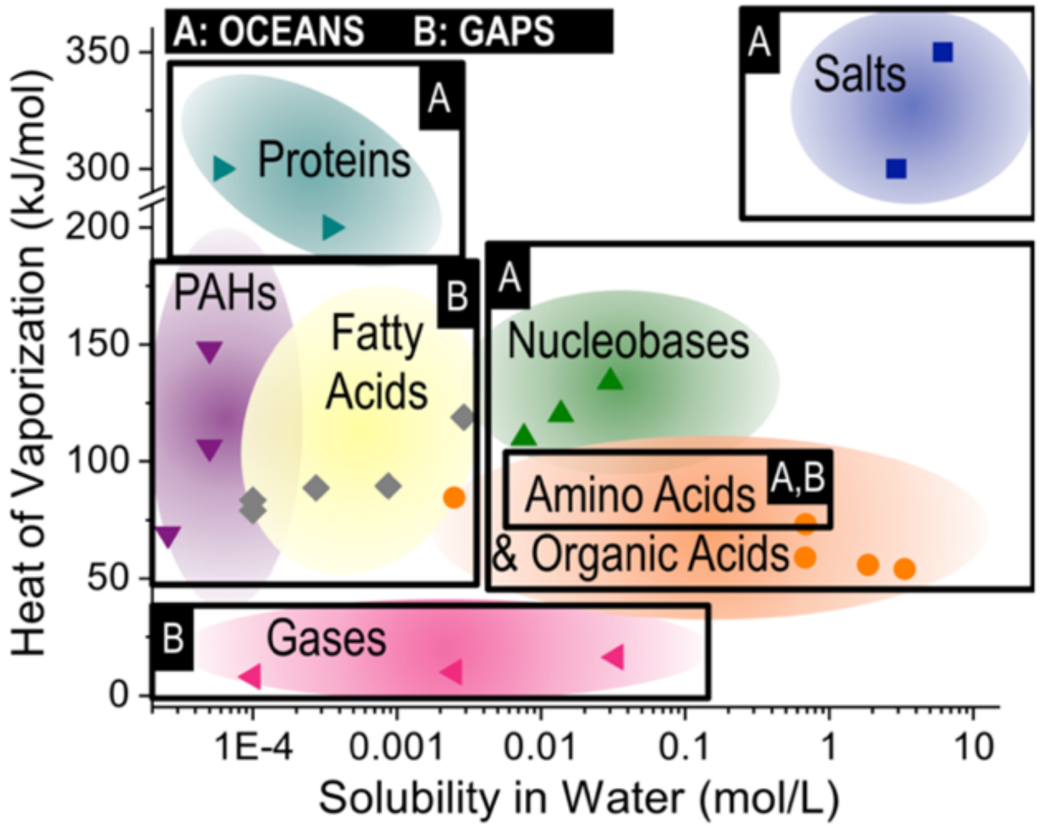
III. OCEANS



I. Architecting An Organic Chemical Analyzer for a Europa Lander Mission: EMILI

EMILI Philosophy

Deliver Maximum Europa Science by Casting the Widest Possible Nets in "Molecular Space"



Key & Driving Requirements:

- Must handle gases and liquids
- Must perform separations
- Must perform MS
- Must meet Europa Lander SDT measurement requirements

EMILI chooses **highest TRL hardware** with **lowest development risk** that is **capable of achieving science**

- **NASA Goddard** - MS(MOMA), GC(SAM), Mission Operations
- **NASA JPL** - Liquid Extraction, Electrophoresis
- **NASA Ames** - Spaceflight Microfluidics
- **Honeybee Robotics** - Sample Handling (SAM)

Europan Molecular Indicators of Life Investigation
EMILI = OCEANS + GAPS

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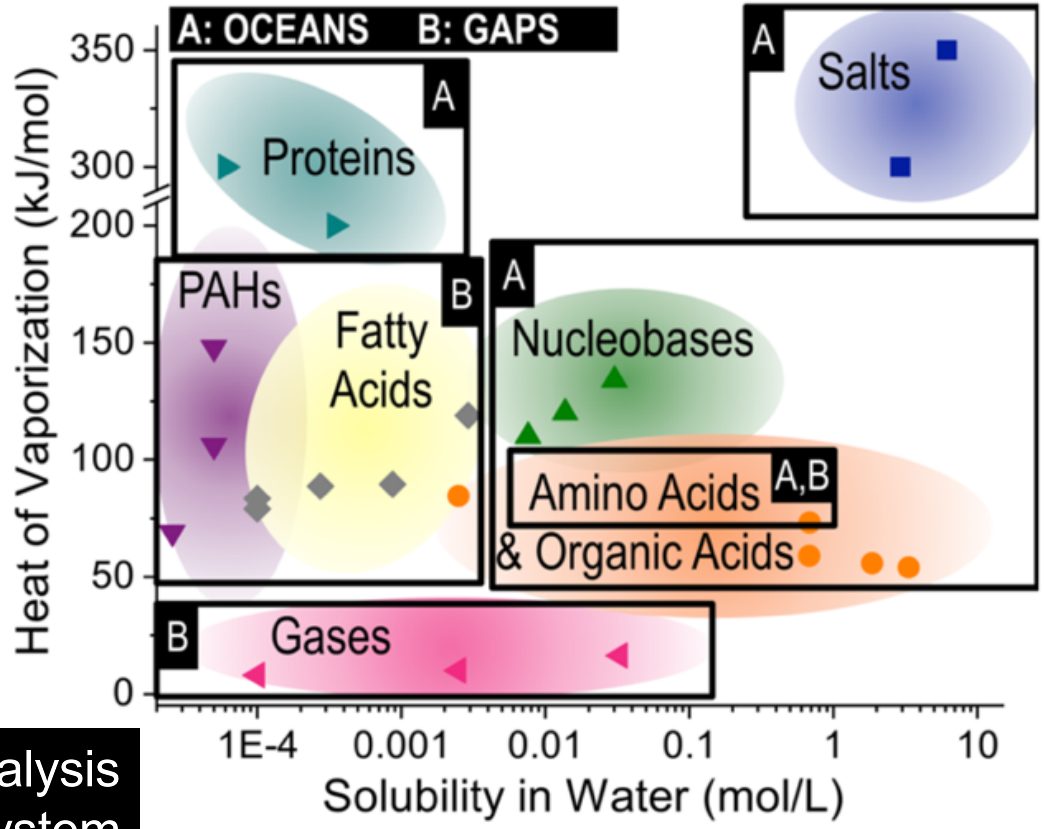
OCEANS - Organic Capillary Electrophoresis Analysis System

NASA JPL
NASA Ames

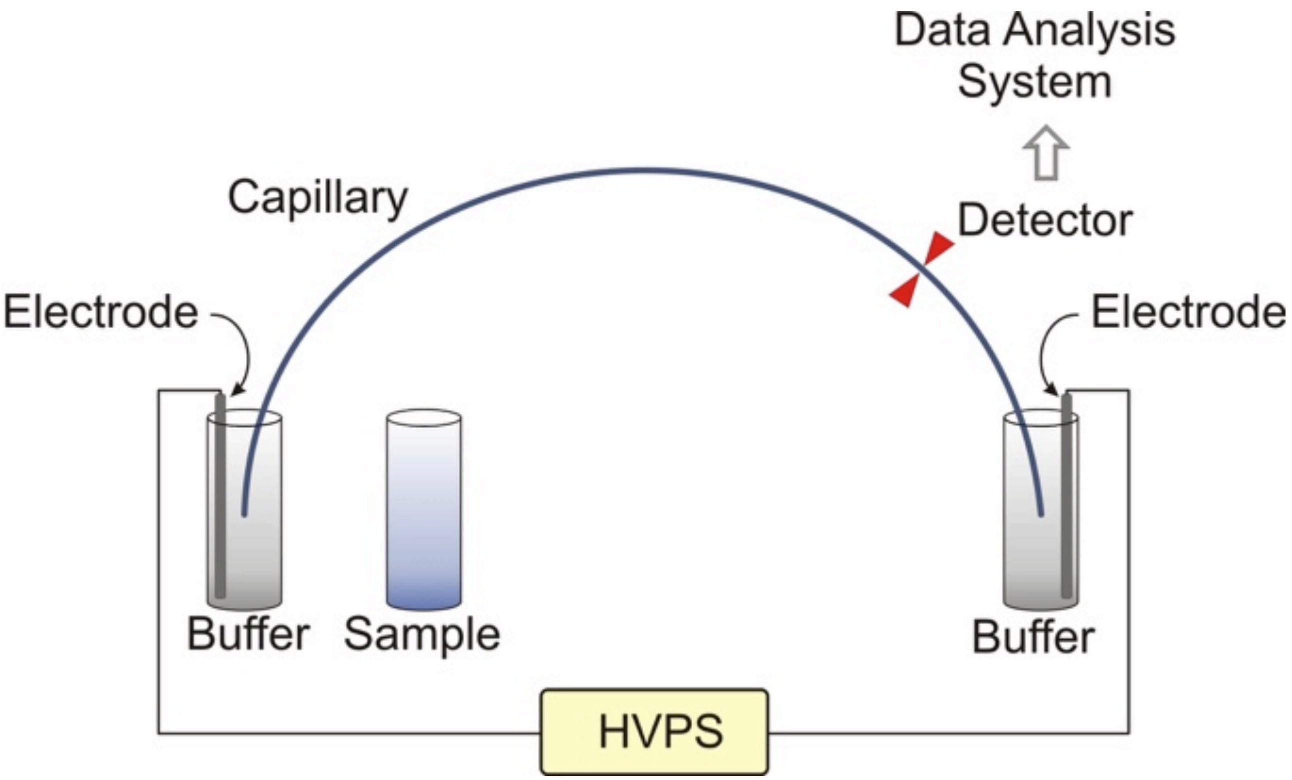


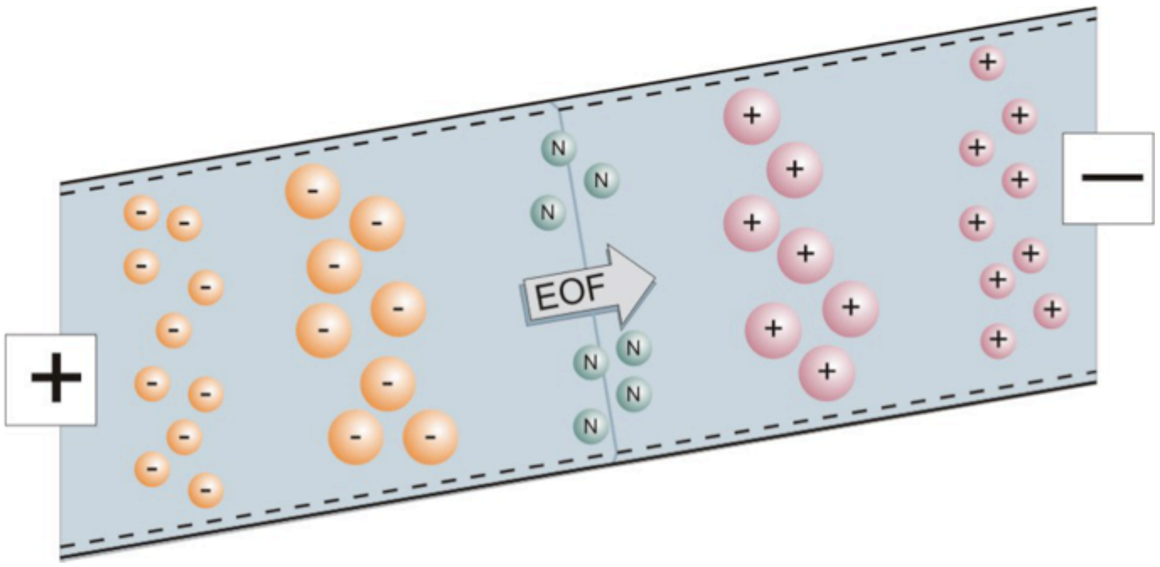
GAPS – Gas Analysis Processing System

NASA Goddard

OCEANS uses Electrophoresis

- Simplest technique for performing liquid-based separation science on a mission
- Has low power, low mass, high sensitivity, high efficiency
- Charged molecules move at different speeds in the liquid
- Various detection modes possible





II. Key Developments at JPL

Most capable published method for amino acid analysis on life detection missions

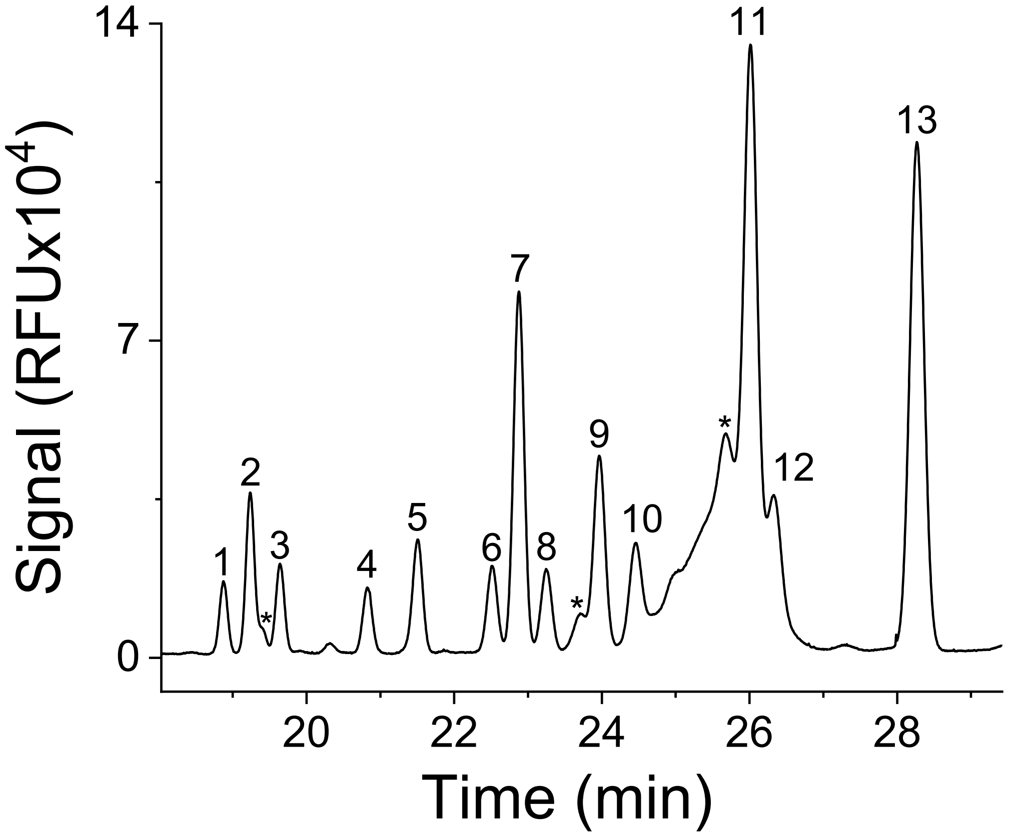
by Jessica S. Creamer, Talk 107-3 Monday, June 24th, 2:00 – 2:15pm

analytical chemistry
Article
pubs.acs.org/ac

Enhanced Resolution of Chiral Amino Acids with Capillary Electrophoresis for Biosignature Detection in Extraterrestrial Samples

Jessica S. Creamer, Maria F. Mora, and Peter A. Willis*

LODs now down to 1 nM



Peaks:
1. D-His
2. D-Leu
3. D-Val
4. L-His
5. L-Leu
6. D-Ser
7. GABA;
8. L-Val
9. D-Ala
10. L-Ser
11. β-Ala
12. L-Ala
13. Gly
*Dye side products

Creamer et al. Anal. Chem. 2017, 89, 1329–1337

In Situ Chemical Analyzers in Development at JPL

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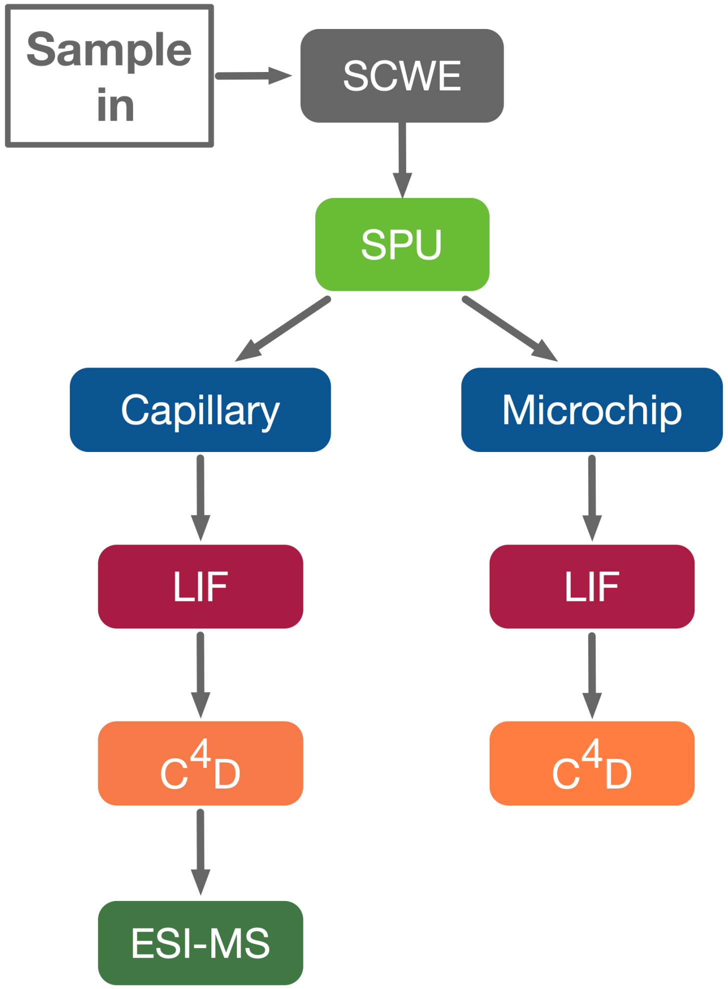

LEGEND

- Subcritical water extraction: Extracts organics from the sample
- Sample processing unit: Characterizes sample and prepares it for analysis
- Capillary/microchip electrophoresis: Separates sample into components
- Laser-induced fluorescence: Detects labeled amino acids at nanomolar concentrations
- Contactless conductivity: Detects any charged species, inorganic and organic ions
- Electrospray ionization-Mass spectrometry: Detects a broad range of organic species

In Situ Chemical Analyzers in Development at JPL

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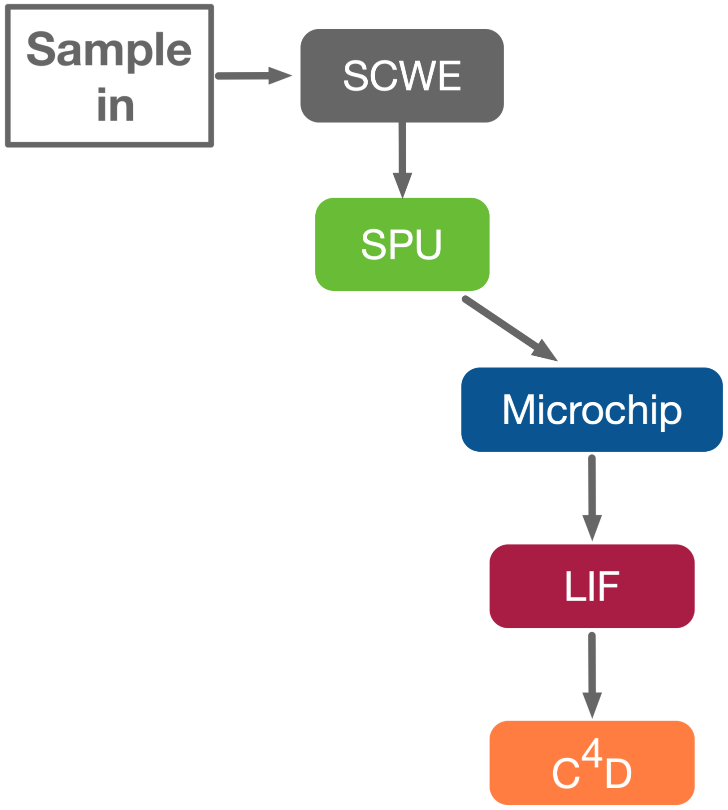

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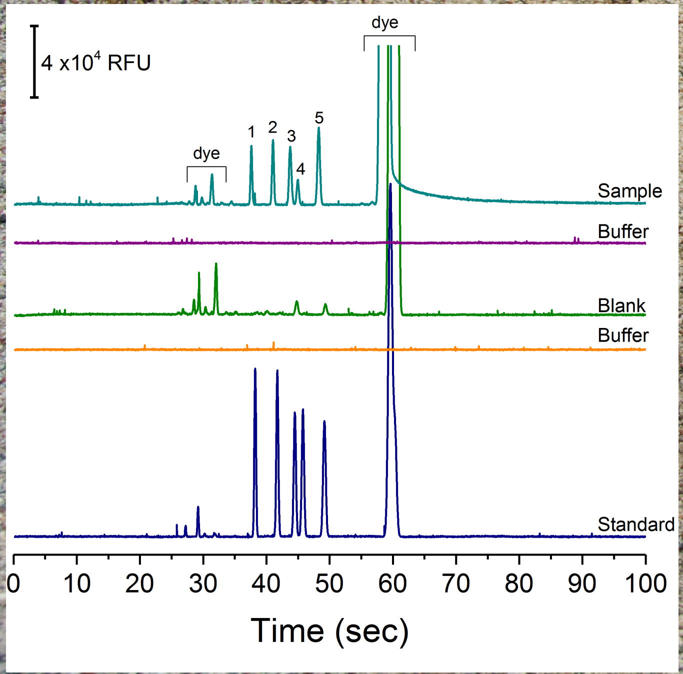
Chemical Laptop

Propulsion Laboratory
rnia Institute of Technology

First portable and fully automated ME-LIF instrument



Portable & Automated Extractor

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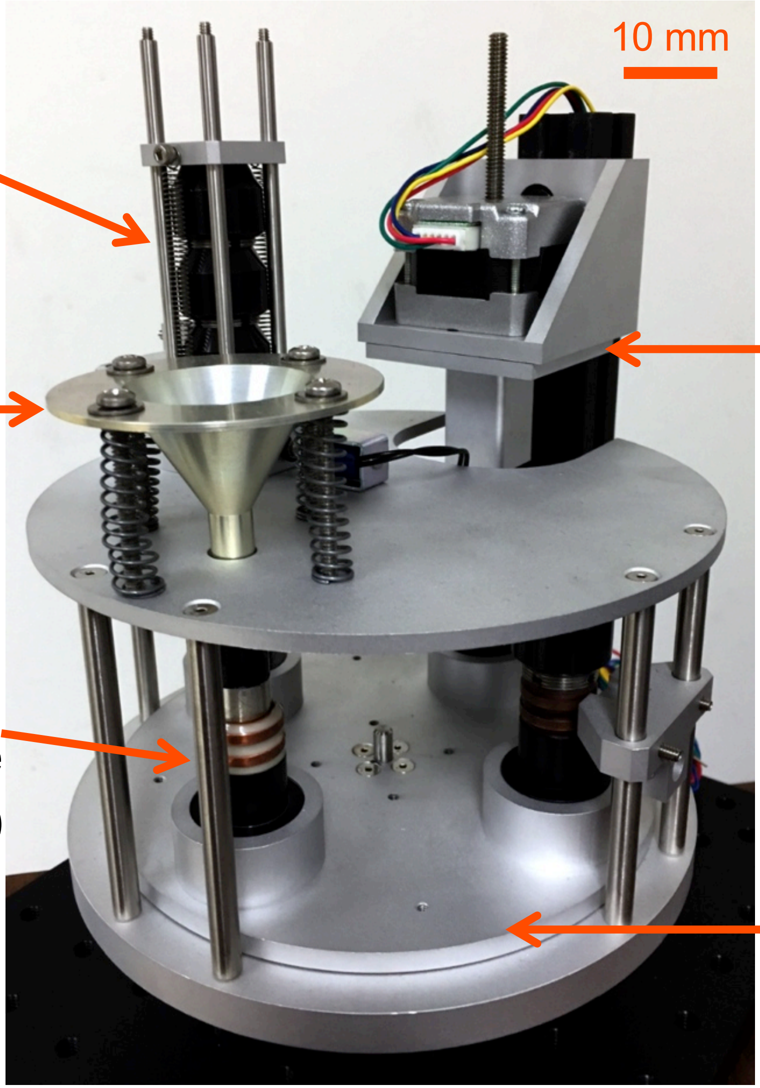

Kehl F. et al., J. Geophys. Res., in preparation, 2019.
NTR 51154, Patent pending.

Biosignatures in the Atacama Desert

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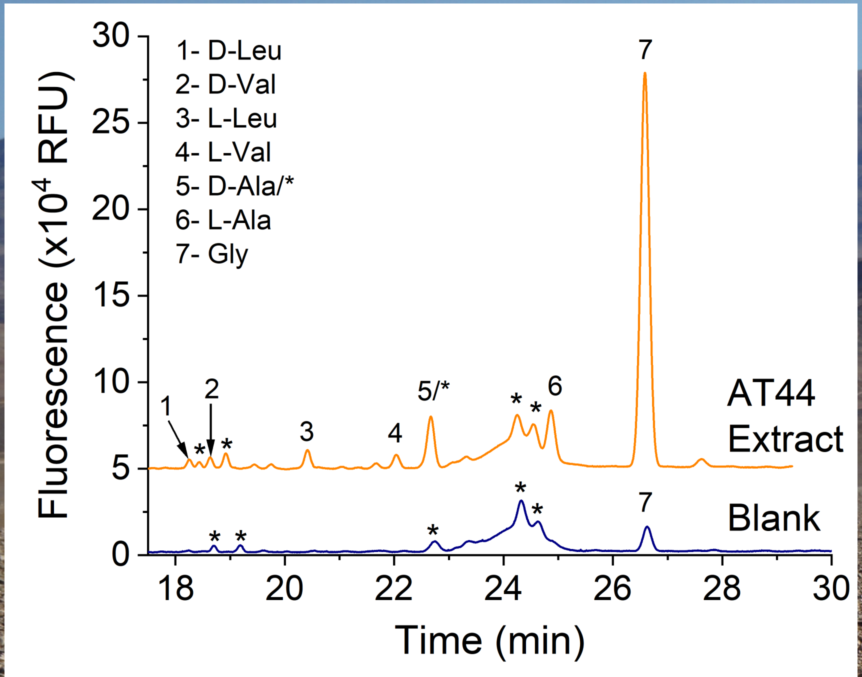
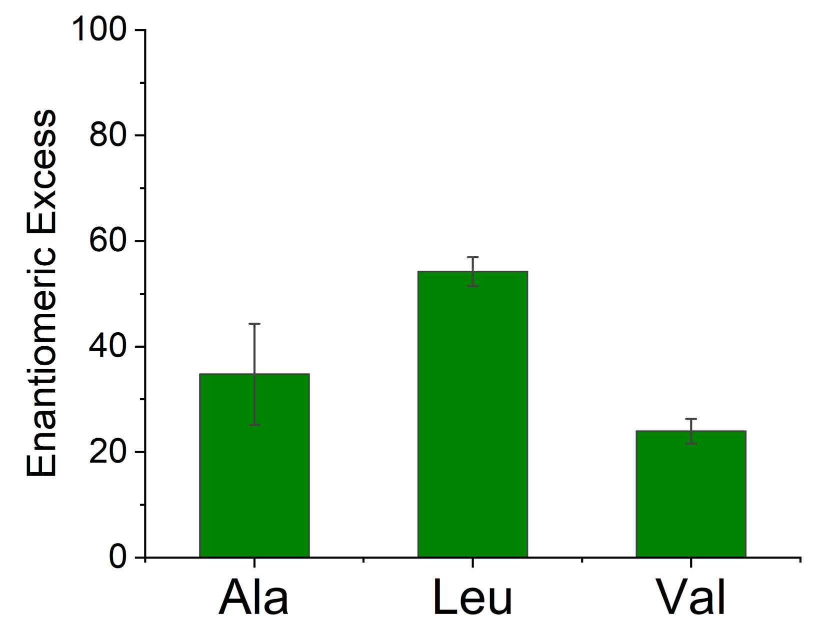
California Institute of Technology

Do not need desalting
Do not need preconcentration
Just analyze fluid from extractor directly





Kehl F. et al., J. Geophys. Res., in preparation, 2019.

Next: Validation in the Field

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Atacama Desert – September 2019

Extractor

Chemical Laptop

III. OCEANS

In Situ Chemical Analyzers in Development at JPL

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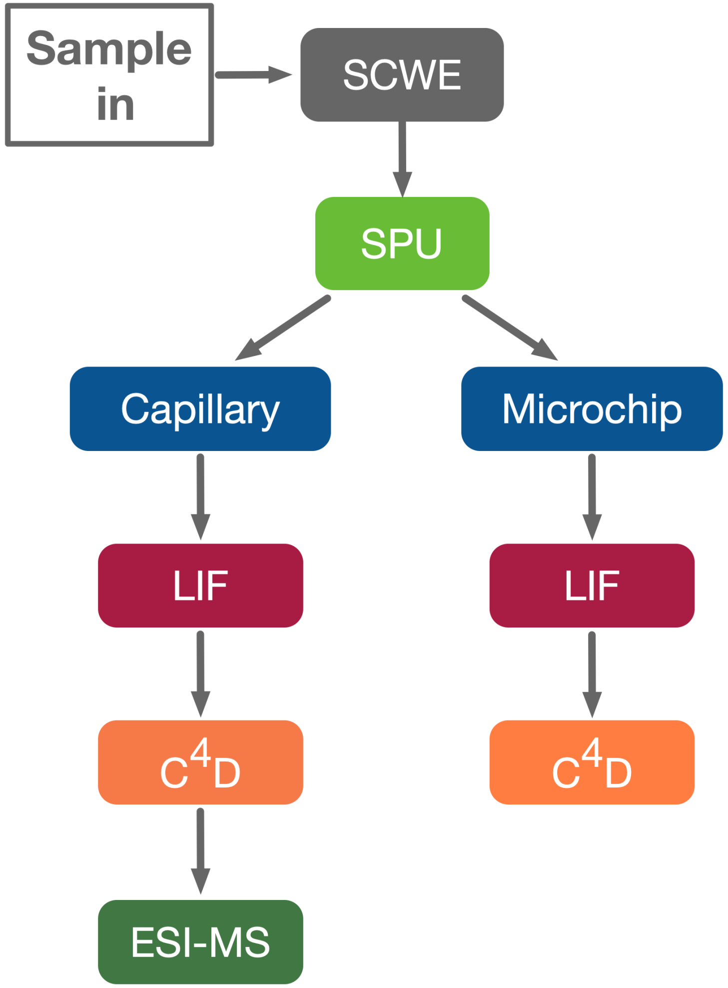

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In Situ Chemical Analyzers in Development at JPL

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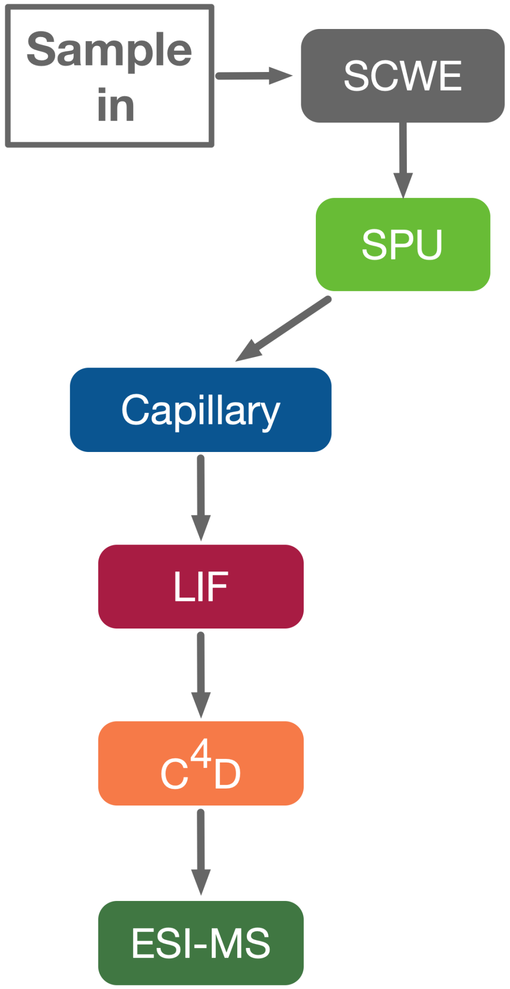
OCEANS



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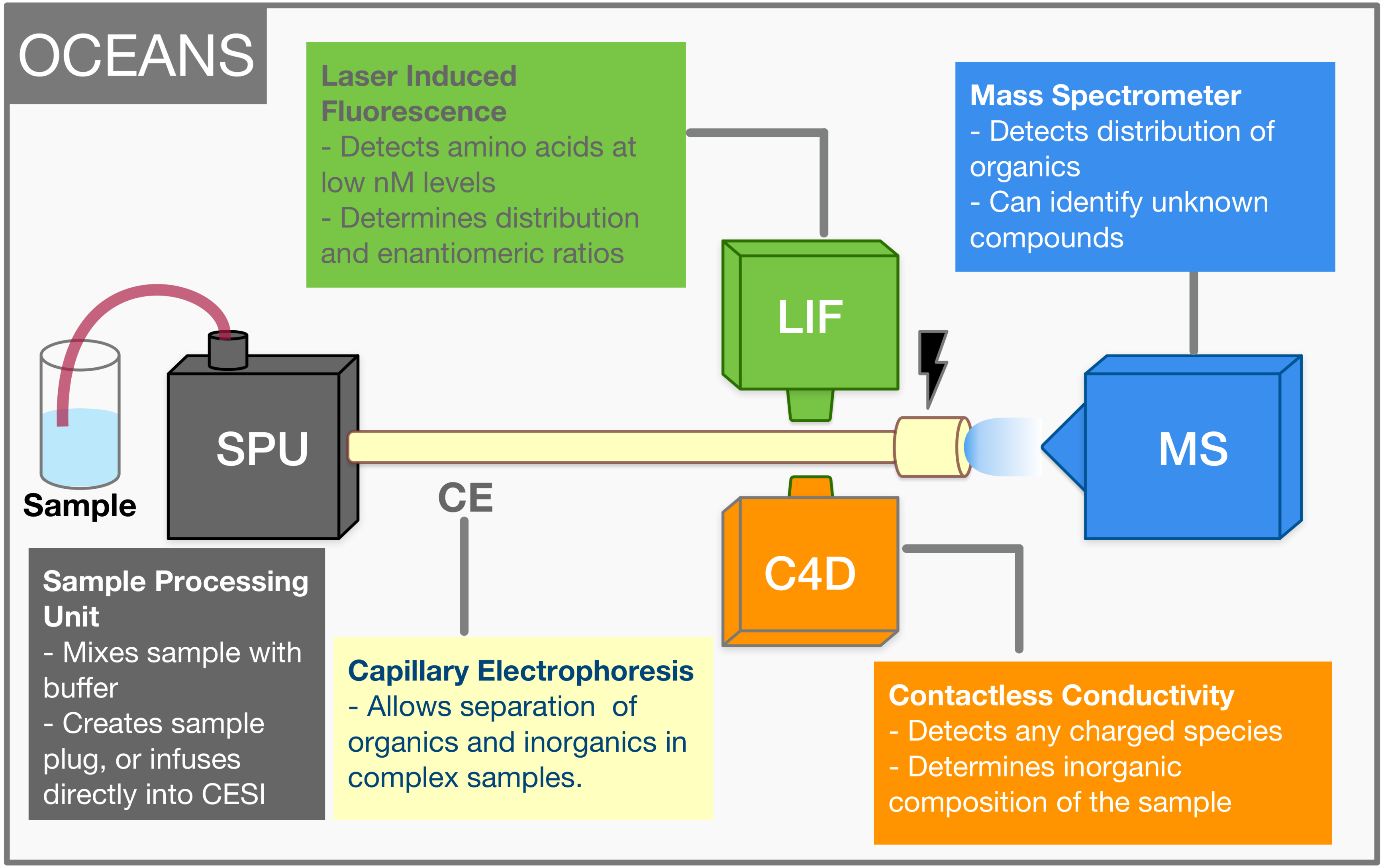
Organic Capillary Electrophoresis Analysis System (OCEANS)



Coupling to mass spectrometry

Coupling to MS is essential in discovering “unknown unknowns” on life detection missions.

This leads us to select capillary approach.

A robust, spaceflight capable electrospray source that can be interfaced to a spaceflight compatible sample injector is the key missing piece of the puzzle.

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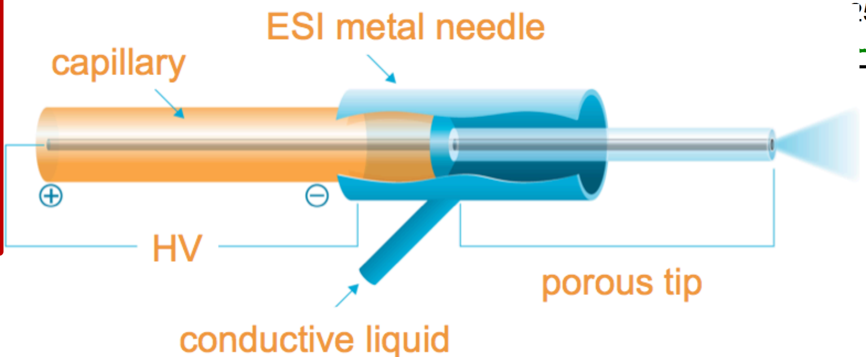
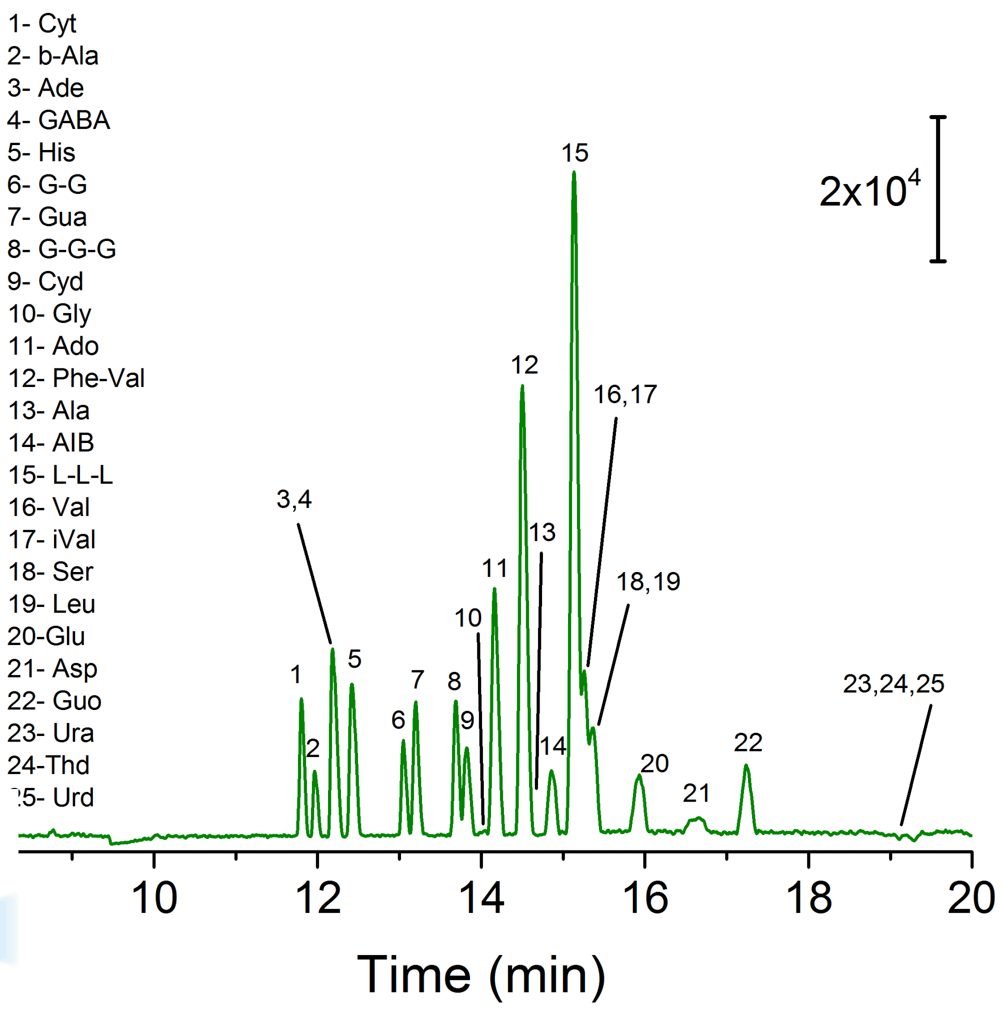
CESI-MS

partnership with SCIEX (Brea, CA) Pioneer / World Leader in CE and CE-MS





OCEANS CE-C4D-ESI-MS

Electrophoresis system for multi-mode detection

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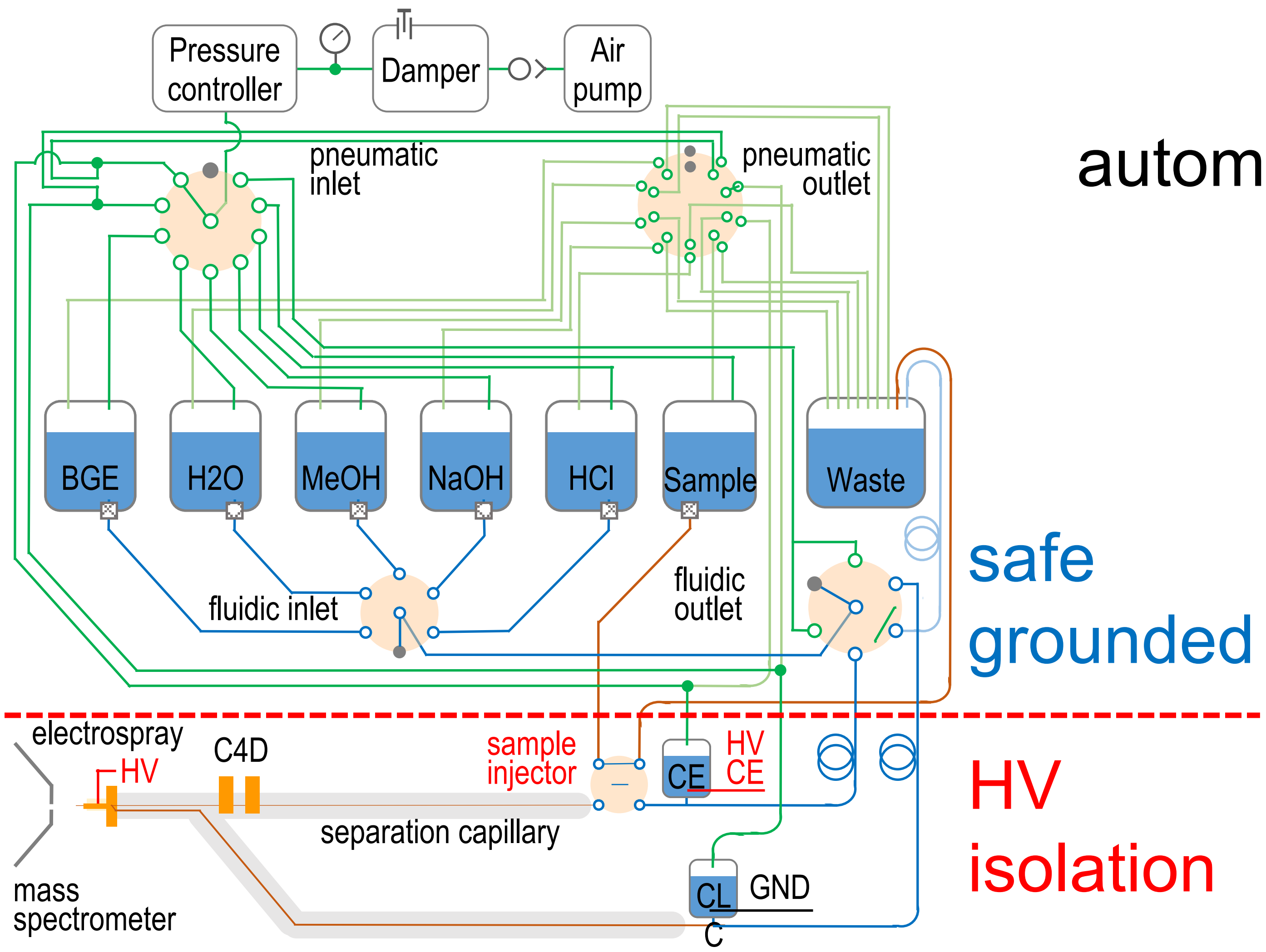
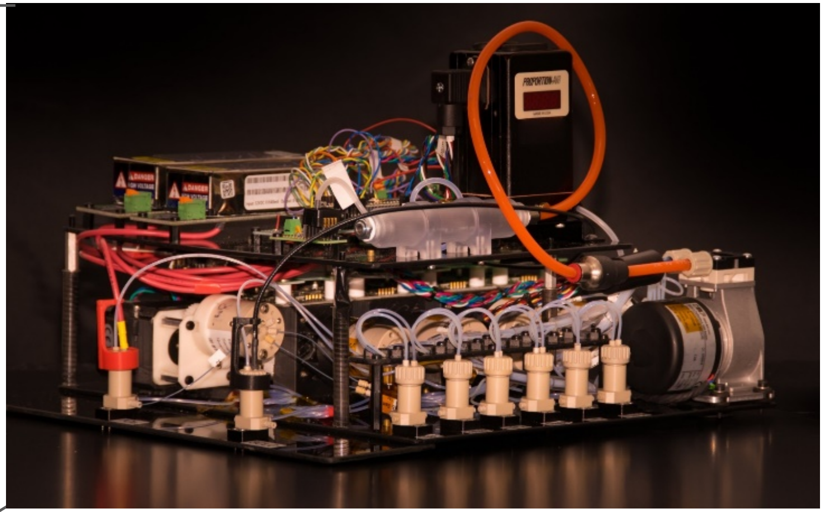


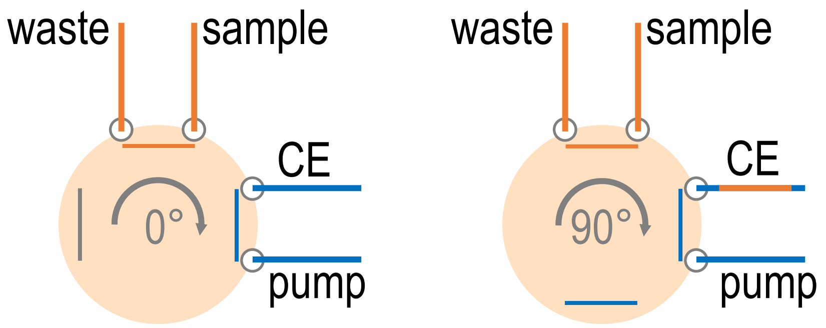
safe grounded

HV isolation

fully automated



precise, reproducible sampling



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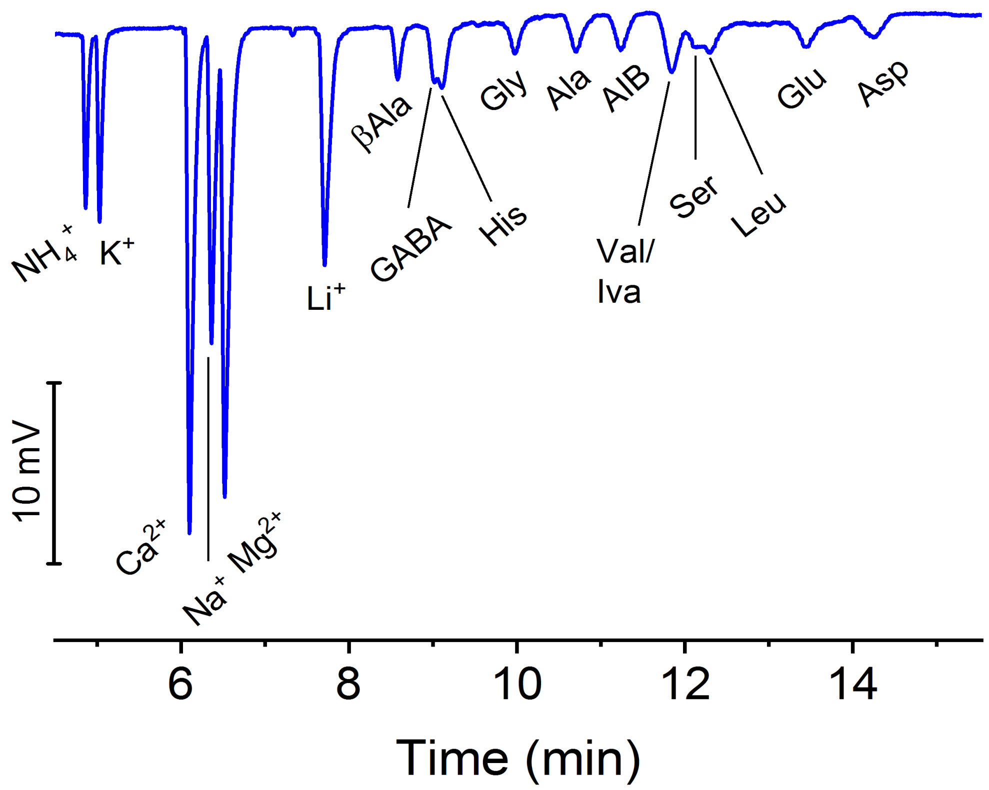
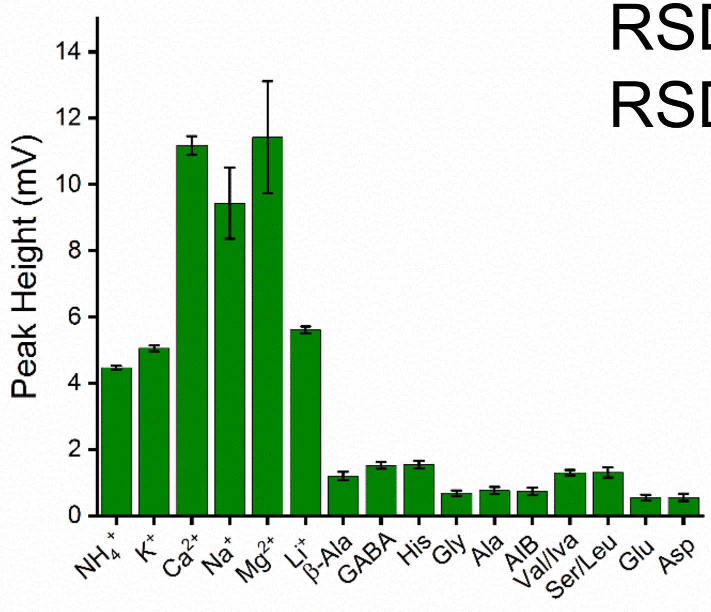
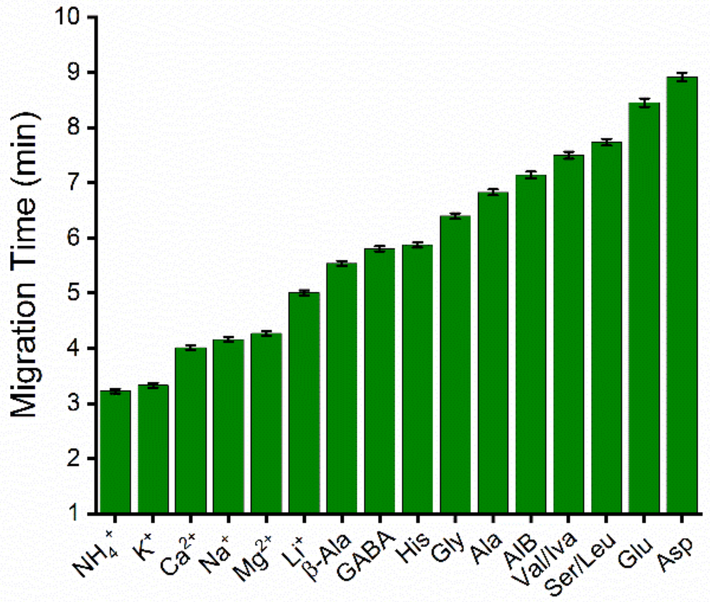
System Validation



Conditions: 250 μM inorganics, 50 μM amino acids; BGE: 5 M acetic acid; injection volume: 8 nL; separation voltage: 20 kV; capillary length: 67 cm (effective: 47 cm); 50 μM I.D. capillary.

Reproducibility (10 runs)
RSD: <1% for migration time
RSD: 1-10% for peak height





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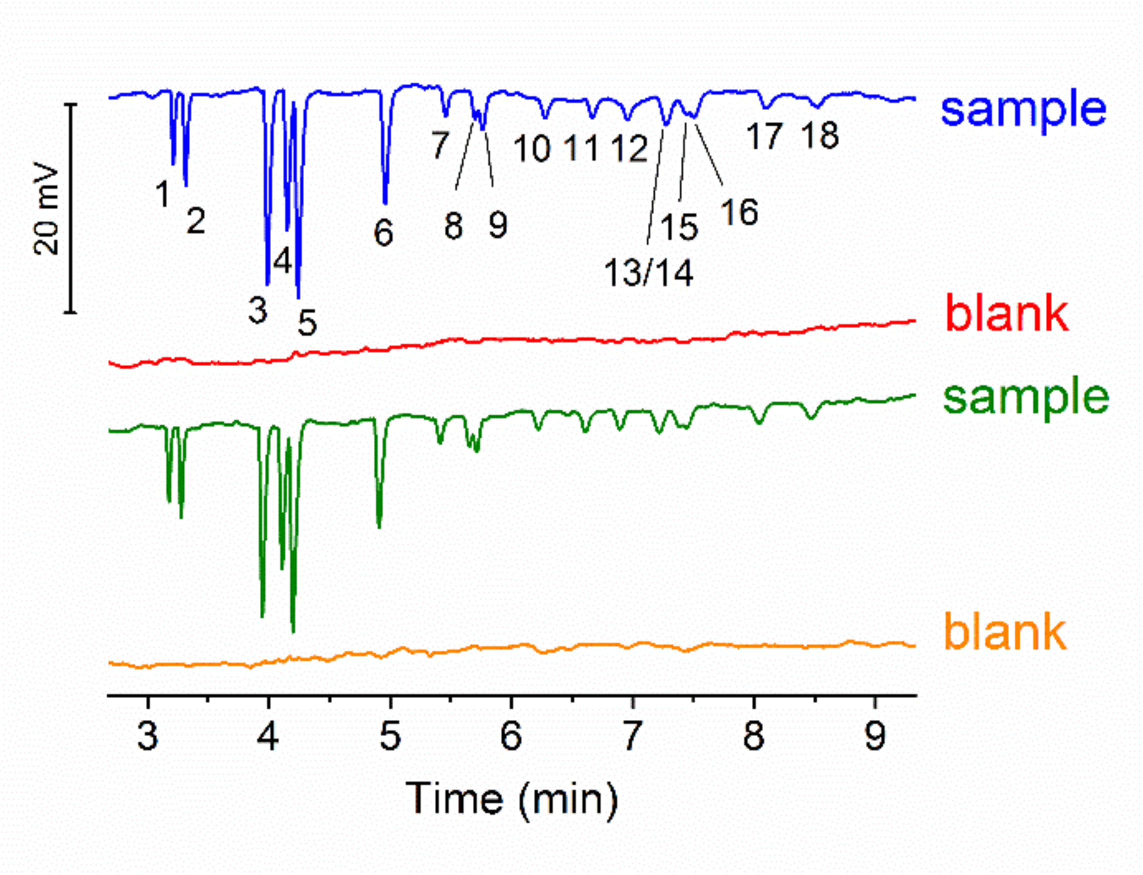
System Validation: Carry Over



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1) NH_4^+
2) K^+
3) Ca^{2+}
4) Na^+
5) Mg^{2+}
6) Li^+
7) β-Ala
8) GABA
9) His
10) Gly
11) Ala
12) AIB
13) Val
14) Iva
15) Ser
16) Leu
17) Glu
18) Asp

OCEANS CE-MS

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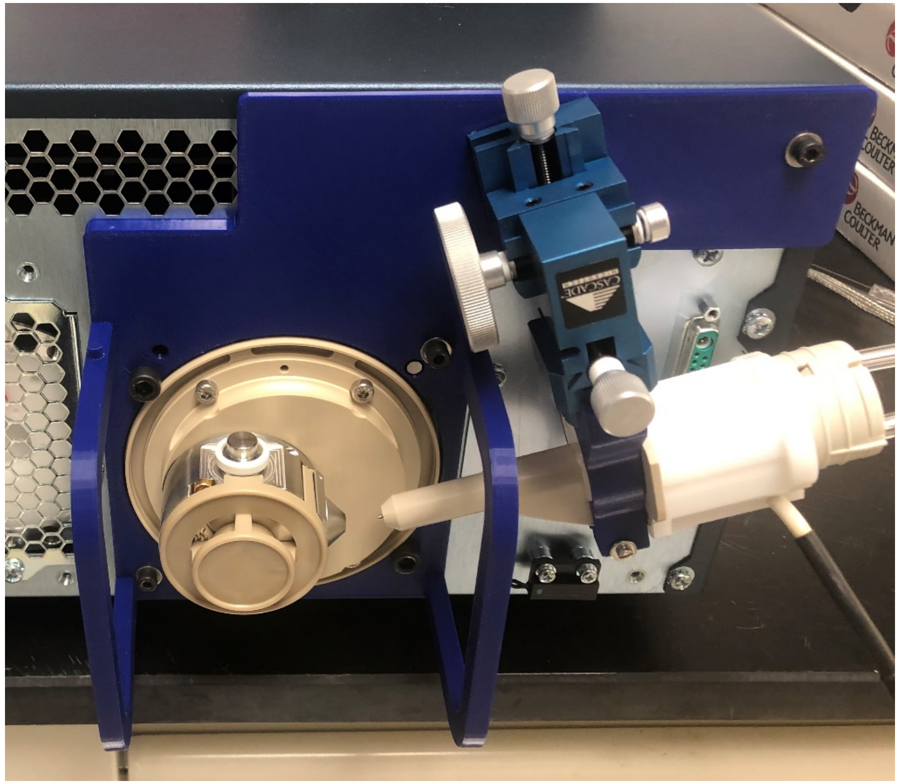
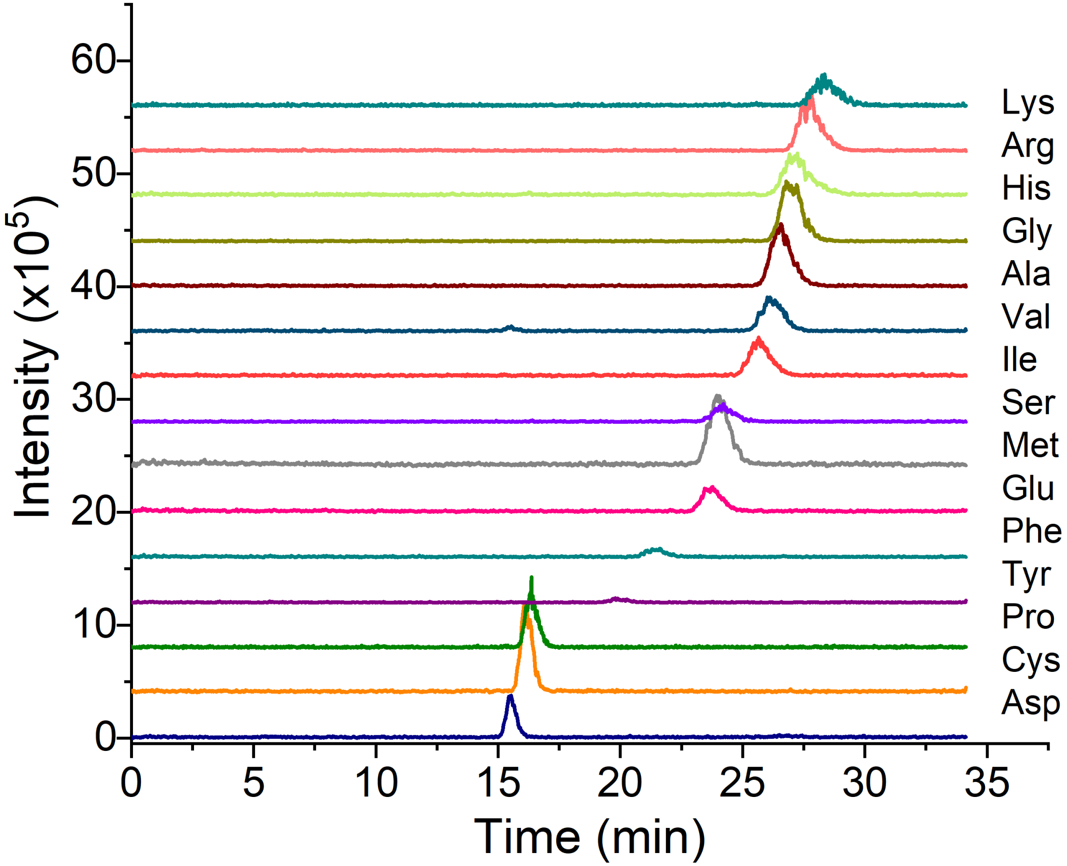


- portable MS (Waters QDA) with SCIEX nanoelectrospray

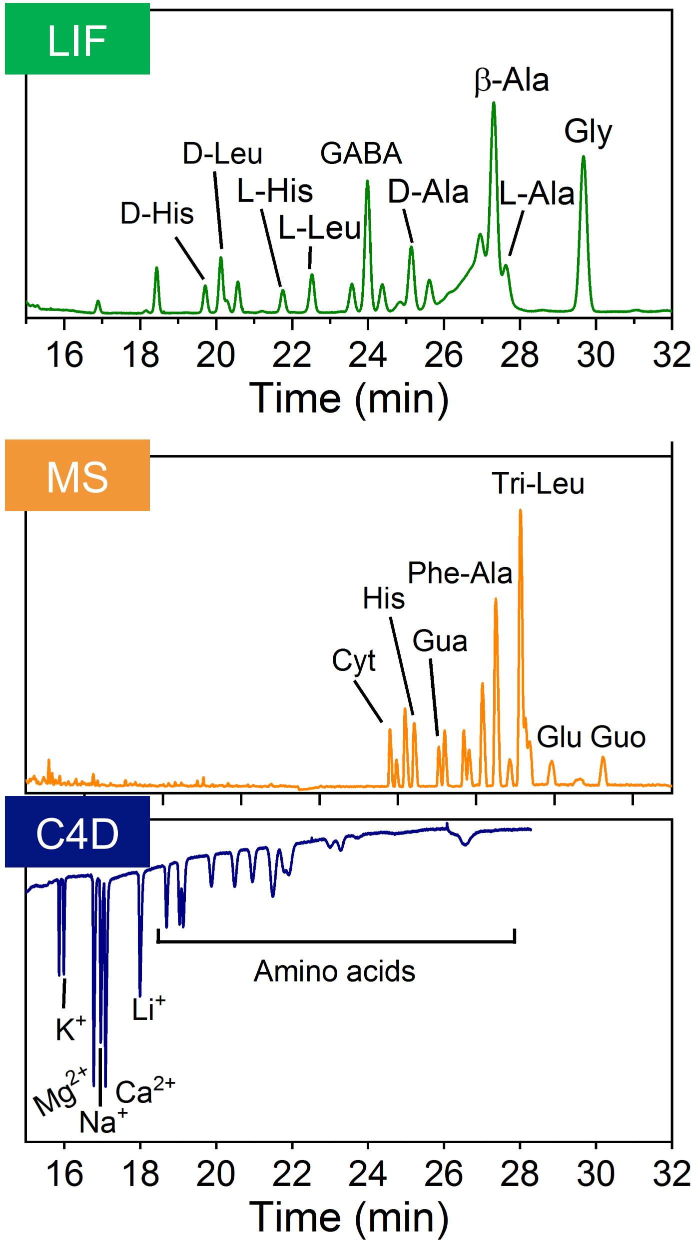
- overlay of extracted ion chromatograms



Conditions: 50 µM amino acids; BGE: 10% acetic acid; injection volume: 8 nL; separation voltage: 20 kV; pressure: 5 psi; capillary length: 90 cm; 50 µM I.D.; spray voltage: 1.5 kV.

OCEANS Science Traceability

Goal	Objectives	Investigations
Search for evidence of life on Europa	A: Detect and characterize any organic molecular indicators of past or present life	**A1:** Determine the types, relative abundances, and enantiomeric ratios of amino acids (AAs)
		A2: Determine the abundances and patterns (i.e., population distributions) of organic compounds in the sampled material, with an emphasis on identifying potentially biogenic characteristics and molecular complexity.
	B: Characterize habitability	**B1:** Characterize the inorganic composition of the sample for sources of energy, chemically reactive species that could degrade biosignatures, or ions that could aid in elucidation of sample origin



Advancing Technology Readiness Level (TRL)

Key TRL Issues [1]:

- end-to-end operational testing,
- system integration,
- component selection and validation,
- sterilization,
- environmental non-operational testing, *particularly radiation* [2]

[1] Willis et al., Analytical and Bioanalytical Chemistry 2015, 407 (23), 6939-6963.
[2] Creamer et al., Electrophoresis 2018 (22), p. 2864-2871. doi: 10.1002/elps.201800274.

Fieldwork

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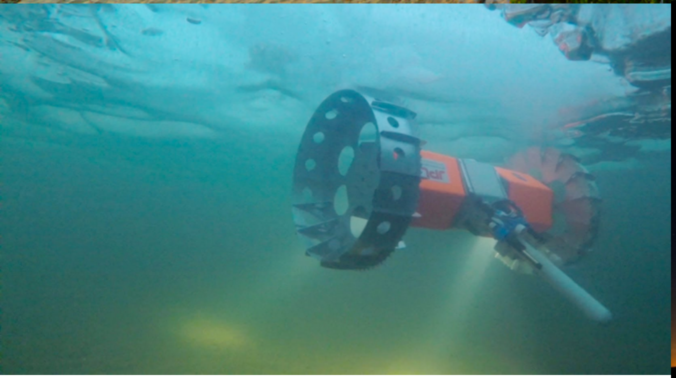


Parting Message

EMILI maximizes the science return of a Europa Lander mission, *and our chances of identifying life, should it be present.*

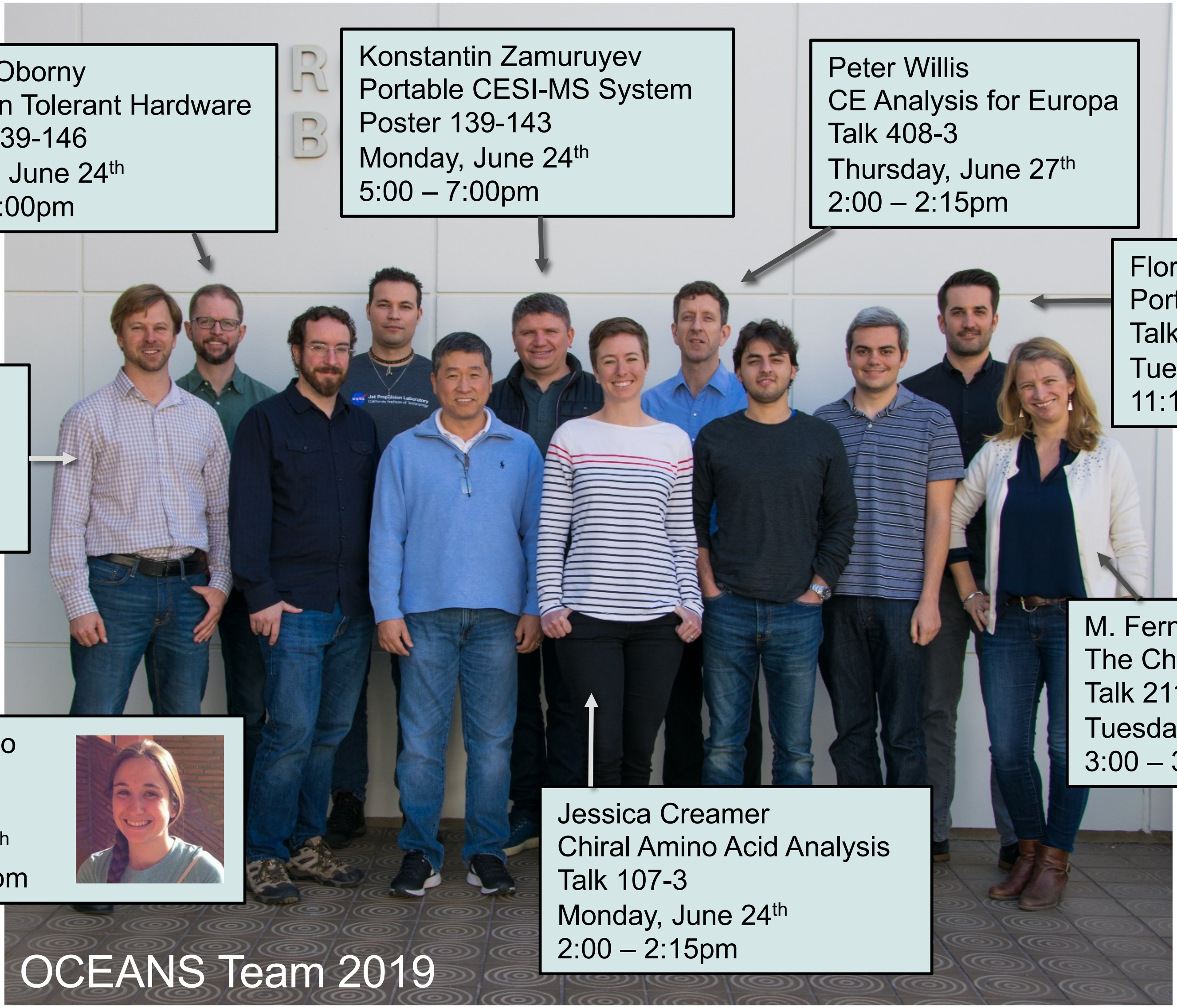
OCEANS has been specifically designed for this purpose using NASA systems engineering processes.

The guiding principle behind our development strategy is the minimization of risk.

Acknowledgements

Jet Propulsion Laboratory
California Institute of Technology

- JPL's Chemical Analysis and Life Detection Group (pictured here)
- Funding from NASA/JPL programs: ICEE-2, JNEXT, PICASSO, NAI, PSTAR, NPP, SBIR, R&TD, TEFIM, Europa Lander SDT
- SCIEX
- The work done in this presentation was done at the Jet Propulsion Laboratory, California Institute of Technology, under a contract with the National Aeronautics and Space Administration.



OCEANS Team 2019

Thank you

Recent Key Publications

“Stability of Reagents used for chiral amino acid analysis during spaceflight missions in high-radiation environments.” Creamer, J., Mora, M.F., and Willis, P.A. Electrophoresis 2018 (22), p. 2864-2871. doi: 10.1002/elps.201800274.

“Enhanced Resolution of Chiral Amino Acids with Capillary Electrophoresis for Biosignature Detection in Extraterrestrial Samples.” Creamer, J. S., Mora, M. F., & Willis, P. A., Analytical Chemistry 2017, 89(2), 1329–1337.

“Extraction of amino acids from aerogel for analysis by capillary electrophoresis. Implications for a mission concept to Enceladus’ Plume.” Mora, M. F., Jones, S. M., Creamer, J. and Willis, P. A. (2017), Electrophoresis 2017. doi:10.1002/elps.201700323

“Methods and Processes for Chiral Amino Acid Biosignature Analysis on Spaceflight Missions”, Jessica Creamer; Maria F. Mora; and Peter A. Willis, NASA NTR #50368, 2016.

“The Chemical Laptop: a Portable, Fully Automated Microchip Electrophoresis Instrument for Future in situ Planetary Investigations”, Peter A. Willis, Maria F. Mora, Florian Kehl, and Nathan Bramall, NASA NTR #50355, 2016.

“Implementation of microchip electrophoresis instrumentation for future spaceflight missions.” Willis. P. A, Creamer, J. S., Maria F. Mora. Analytical and Bioanalytical Chemistry 2015, 407 (23), 6939-6963.

Most Important Older Publications

Jet Propulsion Laboratory
California Institute of Technology

Cable et al., Microchip nonaqueous capillary electrophoresis of saturated fatty acids using a new fluorescent dye. Analytical Methods 2014, 6 (24), 9532-9535.

Cable et al., Identification of primary amines in Titan tholins using microchip nonaqueous capillary electrophoresis. Earth Planet. Sci. Lett. 2014, 403, 99-107.

Mora et al., Analysis of thiols by microchip capillary electrophoresis for in situ planetary investigations. Electrophoresis 2013, 34 (2), 309-316.

Cable et al., Low-Temperature Microchip Nonaqueous Capillary Electrophoresis of Aliphatic Primary Amines: Applications to Titan Chemistry. Analytical Chemistry 2013, 85 (2), 1124-1131.

Mora et al., Microchip capillary electrophoresis instrumentation for in situ analysis in the search for extraterrestrial life. Electrophoresis 2012, 33 (17), 2624-2638.

Mora et al., Toward Total Automation of Microfluidics for Extraterrestial In Situ Analysis. Analytical Chemistry 2011, 83 (22), 8636-8641.

Willis et al., Monolithic photolithographically patterned Fluorocur (TM) PFPE membrane valves and pumps for in situ planetary exploration. Lab on a Chip 2008, 8 (7), 1024-1026.

Aubrey et al., The Urey instrument: An advanced in situ organic and oxidant detector for Mars exploration. Astrobiology 2008, 8 (3), 583-595.

Skelley et al., Organic amine biomarker detection in the Yungay region of the Atacama Desert with the Urey instrument. Journal of Geophysical Research: Biogeosciences 2007, 112 (G4).